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The Na_4^{+3} Clusters in Sodium Sodalite

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Abstract

We have measured and calculated the absorption spectrum of the Na_4^{3+} clusters in $Na_3[AlSiO_4]_3$ sodalite prepared by high vacuum deposition of sodium atoms. The samples with a $Na_4^{3+}:Na_3^{3+}$ cluster ratio up to 1:10 show a single absorption feature with λ_{max}= 628 nm (1.99 eV). The absorption originates from the individual sodalite cages containing Na_4^{3+} cluster. For the $Na_4^{3+}:Na_3^{3+}$ cluster ratio larger than 1:10, when some of the Na_4^{3+} clusters are likely to interact, the changes in absorption spectra indicate the onset of metal-insulator transition. Time dependent quantum mechanical calculations of the photon absorption cross section of Na_4^{3+} clusters in sodalite at infinite dilution were carried out. The dependence of the calculated spectra on sodalite framework charges and cluster geometry was used to determine which of the proposed charge distribution models are consistent with the absorption spectra. The best
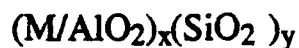
agreement between measurements and calculations is obtained for Na=+1, Si=+1.9, Al=+0.9, and O= -0.95.

I. INTRODUCTION

The AlO_4 and SiO_4 tetrahedra are building blocks of all aluminosilicate zeolites described by:

$$(M/AlO_2)_x(SiO_2)_y$$

M represents an electron donor, usually an alkali metal, whose stoichiometry is determined by the rule that the number of electrons donated to the framework must correspond to the number of aluminum atoms in a given structure. The Al/Si ratio in zeolites varies between $0<x/y<1$ and to a large extent determines their structure and properties. The chemical activity of the zeolite surface is strongly influenced by the charge distribution on the framework. Unfortunately even for the simplest zeolites this distribution is uncertain.

We address this problem for sodalite[1], a zeolite that consists of identical truncated octahedra cages (Fig. 1) of approximately 7 Å in diameter. The single cage stoichiometry is $Na_4[AlSiO_4]_3 X \cdot 2H_2O$. X represents a negative ion (e.g.

OH or halogen) which occupies the center of the cage and has a tetrahedral

coordination with four sodium atoms as nearest neighbors. The silicon and the

aluminum atoms are located at the apexes of the truncated octahedron and are

joined by four tetrahedrally coordinated oxygen atoms. Each cage has six eight-

atom-rings (four tetrahedral metal atoms and four oxygen atoms) and eight

twelve atom rings (six tetrahedral metal atoms and six oxygen atoms), which will

be called here the four and the six metal rings. The four sodium atoms inside

each sodalite cage are coordinated to the three oxygen atoms from the six metal

rings. Sodalite has a cubic symmetry with the $P\bar{4}3n$ space group.

Sodalites are dielectric materials with a band gap of approximately 6 eV[2].

They can be viewed as a heavily "doped" SiO_2 (1:1) with both p-type (Al) and n-

type (alkali metal) "impurities"[3], so that a high probability for trapping charged

particles is expected. If an optically transparent halogen-sodalite, such as Na_4

$[AlSiO_4]_3$ $Cl\cdot2H_2O$, is exposed to high energy electrons or x-rays, a colored

sample is obtained; a phenomenon known as the catodochromic effect.[4] It is

believed that cages with a p-type defect such as negative ion vacancy, i.e. {Na_4

$[AlSiO_4]_3 \cdot2H_2O\}^{+1}$, are responsible for this effect. The electrons formed by the

x-rays are trapped by these defects in the place of the absent negative ion and

form Na_4^{+3} clusters with absorption in the visible region. The 13 peak hyperfine structure of the ESR signal[5] characteristic of these centers indicates the presence of an unpaired electron delocalized over four equivalent sodium atoms. The number of Na_4^{+3} clusters that can be formed in halogen sodalites is limited by the number of negative ion vacancies produced during synthesis.

If one chooses to deposit sodium vapor onto the surface of $Na_3[AlSiO_4]_3$ sodalite, the dehydrated and dehydroxylated form of $Na_4[AlSiO_4]_3 OH \cdot 2H_2O$, the concentration of the Na_4^{3+} clusters can be varied at will. At low Na_4^{3+} concentration, the $Na_3[AlSiO_4]_3$ sodalite is pale blue and produces an ESR spectrum[6] identical to that reported for the catodochromic halogen sodalites. Prolonged exposure of the $Na_3[AlSiO_4]_3$ sample to sodium vapor gives rise to a sequence of colors: light blue - blue - purple - black. This phenomenon has been qualitatively described by Barrer[6], but no quantitative correlation between the spectroscopic data and the Na_4^{3+} concentration has been reported.

Here we present measurements of the absorption spectra of samples with known concentration of excess of alkali atoms. These are compared to model calculations of the absorption cross-section to extract information regarding the

sodalite framework charges. The magnitude of the framework charges in sodalites have been subject of disagreement.[7-10] They vary between the covalent scheme[7] which places only a fractional negative charge on oxygen to balance the +1 charge of the Na atoms, and the much stronger ionic model of Skoczyk[10] which places a +3.03 charge on the Si atoms, +2.45 on the Al, and -1.62 on oxygen.

II. THEORETICAL

We outline here how time dependent quantum mechanics is used to calculate the absorption cross section for a model that mimics the properties of an alkali atom absorbed in the sodalite structure. The details will be published elsewhere.[11]

In the infinitely dilute limit, the excess alkali is a single site impurity which contains one electron in excess of a closed shell. In the model used here, this electron interacts through a simple pseudopotential with the excess Na ion and the framework ions. The observable that we calculate is the absorption spectrum of the excess electron. The calculations connect the framework charges to the absorption spectrum.

We assume a rigid $Na_3[AlSiO_4]_3$ sodalite framework surrounding the single $Na_4[AlSiO_4]_3$ sodalite cage. The electron position operator is denoted by **r** and the sodalite atoms are located at the position $\{R\}$ with the effective charges $\{Q\}$. The electron momentum is **p**. The Hamiltonian

$$H = p^2/(2m) + V(r;\{R,Q\}) \tag{1}$$

contains the kinetic energy of the electron plus its interaction energy with the framework atoms.

The formula used to calculate the absorption cross section is similar to the one used by Heller[12],

$$\sigma(\omega) \propto \omega \text{Re} \int_0^\infty dt \, \exp(i\omega t) \, C(t). \tag{2}$$

The overlap integral

$$C(t) = \exp(iE_g t/h) \, \langle g| \, \varepsilon \cdot r \, \exp(-iH \, t/h) \, \varepsilon \cdot r |g\rangle, \tag{3}$$

where |g> is the ground state of the electron of energy E_g, and ε is the polarization vector of the light. In Eq.(3) the dynamics of the excess electron is treated explicitly and the light is coupled to the system through the electron dipole operator (i.e. the electron position operator). This formulation provides the spectrum for all the excited states in one calculation without requiring any quantum chemistry input. This is possible for the present example because, by using pseudopotentials to describe the electron-atom interactions, we have an one electron problem.

In practical calculation we cannot propagate the wave function for an infinite time. We use a "window" function $\exp[-(t/\tau)]$ in Eq (2), which cuts off the time evolution of the overlap integral for times substantially longer than τ. With this window function, Eq.(2) generates[12,13] a low resolution version of the true spectrum. The absorption lines aquire a width of the order $\Delta\omega=2\pi/\tau$. Conversely, a spectrum taken with a resolution $\Delta\omega$ contains information about the motion of the excited electron for the time $\tau=2\pi/\Delta\omega$.[12]

One purpose of these calculations is to examine whether the absorption spectrum is sensitive to the charge distribution on the zeolite framework. The interaction between the excess electron and a zeolite atom at position R_i with charge Q_i is given by

$$V(r;\{R,Q\}) = \sum -e^2 Q_i \exp[-(|r-R_i|/\lambda)^n] / \min[|r-R_i|,R^c_i]. \qquad (4)$$

Here e is the electron charge and R^c_i is a cutoff distance used to truncate the coulomb potential. We have included the long range exponential cutoff, $\exp[-(|r-R_i|/\lambda)^n]$, to simplify the coulomb potential at large distances. In the calculations presented here, we use λ = 15.0 - 25.0 Å and n = 4. In order to calculate the interaction potential we use a grid that extends out to a maximum of 22.7 Å from the grid center and covers three zeolite cages in each direction. The values of R^c_i are chosen such that the two body interaction between the electron and i-th atom approximates the ionization potential of the corresponding ion with charge Q_i.

We calculate the absorption spectra for various framework charges proposed in the literature,[7-10] and for several Na-O distances.

III. EXPERIMENTAL

Sodium-hydroxy sodalite, $Na_4[AlSiO_4]_3(OH)\cdot 2H_2O$, was synthesized by standard hydrothermal procedure.[15] The NaOH unit was removed from the cages by the Soxhlet extraction to obtain the hydrated form of sodalite, $Na_3[AlSiO_4]_3\cdot 4H_2O$. The unit cell size change between the initial hydroxy-sodalite hydrate, a=8.7342(8) Å[16], and the final hydro-sodalite phase, a= 8.848(1) Å[17], was monitored with a Scintag automated powder X-ray diffractometer. The thermogravimetric analysis of the hydro-sodalite phase gave the expected water loss of 23%. After calcination of $Na_3[AlSiO_4]_3\cdot 4H_2O$ at 450 ^{o}C the unit cell of $Na_3[AlSiO_4]_3$ was determined. The a=9.122 Å value was in agreement with the literature data.[17]

The vacuum apparatus[18] in which the deposition of alkali metals on zeolites was made, is schematically shown in Fig 2. In each experiment 20 mg of hydro-sodalite powder was placed at the bottom of the tantalum boat and evacuated at 450 ^{o}C for 24 hours. The water loss was monitored with the quadrupole mass spectrometer (UTI 100C). During sodium deposition the boat

temperature was kept at 250 °C to allow for faster diffusion of the alkali atoms through the sodalite crystallites. The background pressure was maintained at 1×10^{-7} Torr and the losses of sodium atoms due to the reaction with residual H_2O or O_2 were negligible. A controllable deposition rate of sodium atoms provided by the alkali metal dispensers[19] was the main improvement over the standard procedure.[6] The dispenser consists of a small metal container holding 1.2 mg of sodium in the form of sodium chromate mixed with a reducing alloy (16 % Al and 84 % Zr). The alkali flux produced by the source, when powered by a current stabilized DC power supply, was calibrated by the mass spectrometric measurements. Once the flux was determined, we could deposit known amounts of sodium onto the zeolite surface by varying the exposure time. The sodium source was placed close to the sample, so that only the zeolite surface was exposed to the sodium flux. By assuming that the sodium sticking coefficient is equal to unity, this approach provides an estimate of the concentration of the excess of sodium atoms in the sodalite sample. After deposition, the sample was transferred, by 180° rotation of the sample holder, into a 3x8x25 mm rectangular quartz tube which is immediately sealed. The tube contains 100 mg of dehydrated $BaSO_4$. Diffuse reflectance spectra of the well homogenized $BaSO_4$ - sodalite mixture were obtained in the region between 240-850 nm using a

computer controlled Cary-14 digital spectrometer with the $BaSO_4$ coated integrating sphere attachment. The diffuse reflectance spectra were corrected for instrumental response using $BaSO_4$ as reference.

IV. RESULTS AND DISCUSSION

A. The absorption spectra of Na_4^{+3} clusters in sodalite

A series of diffuse reflectance spectra corresponding to different concentrations of Na_4^{+3} centers in sodalite are shown in Fig. 3, along with the Na_4^{+3}/Na_3^{+3} concentration ratios. For the first two samples with an excess of one Na atom per 50 and 10 $Na_3[AlSiO_4]_3$ cages, the UV-VIS spectrum is dominated by a broad absorption band centered at 628 nm. We ascribe the origin of this band to the electronic transition of a single unpaired electron trapped by four positively charged sodium atoms, forming a Na_4^{+3} cluster inside the sodalite cage. The shape of this band does not change significantly with increase of the alkali concentration, except for an increase in intensity.

The overall shape of the spectrum is similar to the absorption of the F centers in chloro-sodalite (λ_{max} =530 nm) formed upon its exposure to a high

energy electrons.[21] Spectra of the F centers in halogen-sodalite and that of Na

doped $Na_3[AlSiO_4]_3$ sodalite are similar because in both cases the Na_4^{+3} clusters

are responsible for the absorption. They differ in absorption maxima because in

halogen-sodalite the Na_4^{+3} clusters are surrounded by the cages containing the

$(Na_4Cl)^{+3}$ clusters, while in sodalite case the surrounding cages contain Na_3^{+3}

clusters. This, together with the substantial difference in the unit cell size between

these two structures (0.24 Å) is likely to be responsible for the 100 nm shift

observed in the absorption maxima.

A question that has not been addressed previously is the origin of the large

width of the absorption band of the alkali doped sodalite which is on the order of

1.5 eV (FWHM). In Fig. 4(a) we show the calculated absorption spectrum of an

isolated Na_4^{+3} cluster, consisting of a narrow absorption band centered at 388 nm

(3.2 eV). The computed spectrum of the same cluster inside of the sodalite is

shown in Fig. 4b. The spectrum is calculated[11] for a particular polarization of

light with respect to the oriented single crystal of $Na_3[AlSiO_4]_3$. The additional

absorption features in Fig. 4(b) appear because of interaction of the electron with

the $Na_3[AlSiO_4]_3$ lattice.

Since the spectral measurements were made on a polycrystalline powder

consisting of randomly oriented microcrystalittes, we must average the computed spectra over all orientations of the electric field polarization. We must also average over the orientations of the Na_3 groups inside the sodalite cages. This was done by a Monte Carlo procedure with the final cross section calculated as $\sigma(\omega)=(1/N)\Sigma\sigma_n(\omega)$. The individual cross sections $\sigma_n(\omega)$ correspond to a specific Na_3 orientation. The orientation averaged spectrum for the particular framework charge distribution (Si=1.9, Al=0.9, O=-0.95, and Na=1.0) is shown in Fig. 4(c). The spectral width of the orientationally averaged spectrum is in qualitative agreement with the experimentally obtained one shown in **Fig. 3**.

A particle in a one-dimensional box model was used previously to explain the appearance of the visible absorption in alkali doped sodalites.[6,20] With an estimate of 600 nm for the absorption maxima of the blue colored sodium-doped sodalite, Barrer[6] calculated l=7.4 Å for the length of the box. Our experimental value of 628 nm would give l= 7.57 Å. Although these numbers are not far from the size of the sodalite cage based upon the crystallographic data (~ 7 Å), the agreement is fortuitous. If we improve the particle in a box model, by using a particle confined in the sphere, the agreement with the experiment is much worse. This suggests that particle in a box models cannot be used as a substitute for the potential experienced by an electron inside the zeolite cage.

The blue sample, corresponding to a concentration ratio of 1:4 in Fig. 3, has an additional absorption band at the high energy end of the spectrum. The onset of a weak UV absorption band at ~ 250 nm (5 eV) can be observed in the absorption curve corresponding to the "light blue" sample with Na_4^{+3} / Na_3^{+3} ratio of 1:10. The band expands toward the IR region as the concentration of the Na_4^{+3} centers increases and continuous absorption throughout the entire 200-850 nm region quickly sets in.

This is illustrated in Fig. 5 where the normalized absorption curve of the 'light blue (1:10) sample was subtracted from the spectra corresponding to the blue (1:4), purple (1:2) and the black (>1:1) sample. Subtraction was intended to remove the contribution of the absorption due to the isolated Na_4^{+3} clusters. The shift of the absorption edge shown in Fig. 5 is actually responsible for the sequential color transformation found in alkali-doped sodalites. The initial light blue color of the sodalite is a consequence of the broad λ_{max}= 628 nm absorption band with short wavelength onset at 420 nm, that leaves the blue portion of the visible spectrum mostly unaffected. Transformation from the blue to the black color is caused by superposition of the UV->IR expanding absorption band which start to appear with a higher concentrations of the excess alkali atoms.

In the sodalite crystal lattice each cage is surrounded by 14 neighboring

cages. Eight surrounding cages are connected through the larger six-metal ring openings while other six cages share smaller four-metal ring openings. Appearance of the UV band, for the Na_4^{+3}/Na_3^{+3} cluster ratio of 1:10, coincides with the appearance of Na_4^{+3} clusters in neighboring cages. This creates a three-dimensional network of quasi-one-dimensional arrays of the Na_4^{+3} clusters. The wave functions of the excess electrons in the neighboring cages containing Na_4^{+3} clusters overlap in the direction of the 6-metal rings; we suggest this overlap is responsible for the appearance of the additional absorption in the UV region.

In Fig. 6 we plot a cut through the potential energy surface felt by the excess electron. The framework charges used to calculate the pseudopotential correspond to the model-d in Table I. Two different cut directions are shown: in part (a) the cut is made along the 4-fold axis (through the four-metal rings) and in part (b) the cut is along the 3-fold axis (through the six-metal rings). We note a significant difference in potential barriers along the two axes implying that the interaction between the electrons in two neighboring Na_4^{+3} clusters takes place mostly through the 6-metal ring openings.

The observations described above suggest the possibility of an insulator to metal transition,[23] caused by the overlap between the wave functions of the

electron wave functions, at certain concentrations of excess sodium atoms. This is in agreement with the changes observed in the ESR spectrum of the alkali doped zeolites [6,20].

B. Influence of the framework charges and Na_4^{+3} cluster geometry on calculated spectra.

The effect of the framework charge distribution and the Na-Na distances in Na_4^{+3} on calculated spectra is examined in detail in reference (11). Here we outline the main results only. The approximation of the interaction potentials for ions in a crystal as being purely electrostatic perturbations due to point dipoles goes back at least to the crystal field theory of Bethe in the 1920's.[22] The quest for finding the appropriate charges has been considerable. Based upon suggestions in the literature, we have examined several charge distributions which are shown in Table I, and are denoted as models a,b,c,d,e, and f. The a-model has the weakest framework charge that we consider. We examine it since it was obtained by a widely used procedure to evaluate the electric fields in zeolites.[7] The SiO_2

framework is regarded as being neutral and formal negative charges are distributed on the oxygen atoms upon the substitution of Al for Si. The alkali counter ion takes on a +1 charge to maintain charge balance with the fractional -0.25 charge on the oxygens. The b-model is our interpolation between the a-model and the c-model from Leherte, et. al.[8] who use Muliken ab initio STO-3G atomic net charges to suggest that in ferrierite zeolite there is a +1.5 charge on the Si atoms. The d-model is from Van Genechten, et. al.[9] who use electronegativity equalization methods to obtain a +1.9 charge on the Si atoms in sodalite along with -0.95 charge on oxygen as noted in Table I. The e model is our interpolation between the d-model and a much stronger charge model suggested by Skoczyk[10] which places a +3.03 charge on the Si atoms, +2.45 on the Al, and -1.62 on the oxygen.

Fig. 7 shows the calculated spectra for the charge distributions b,c,d, and e (Table I) respectively for a selected polarization direction. This progression of charge distributions corresponds to increasing the magnitude of charge on the Si, Al and O atoms while maintaining overall charge neutrality as well as Na=+1 charge. A change in the sodalite framework charge alters the energy levels, the oscillator strengths and the spatial distribution of the electron. Here we used d=2.401 Å for the distance between Na and the center of the cage, a fixed Na_3 group orientation, and a fixed polarization direction of the monochromatic light.

Our calculation shows that there is virtually no difference in calculated spectra between the models a and b. For model-c some of the absorption features are being shifted toward the lower energy end of the spectrum for a fraction of eV. From this point on (Si=+1.5, Al=+0.85) the calculated spectra became strongly dependent upon a slight increase of the framework charges and quickly reach the point of a complete spread of the absorption features over the entire spectral region (model e). An instructive parameter to follow is probability P of finding the electron within the volume that approximately corresponds to the size of the sodalite cage (see data in Table I). With the increase of the framework charges the excess electron becomes increasingly delocalized but the probability of finding it within the sodalite cage for model-d (Si=+1.9, Al=+0.9) are still very large; P = 0.95. Any further charge increase however leads to a quick delocalization of the electron over the neighboring framework ions so that for model-e (Si=+2.2, Al=+1.3) P is only 0.05. This allows us to set the upper limit of the charge distribution in sodalite as Si<+2 and Al<+1, O> -1, Na=+1.

The actual Na distance from the center of an isolated Na_4^{+3} cluster in $Na_3[AlSiO_4]_3$ sodalite matrix can not be obtained by structural analysis. Because of that, all our preliminary calculations used a value of d=2.401 Å obtained from the crystal structure of dehydrated hydroxy-sodalite.[23] In Na_4^{+3} cluster the

negatively charged OH ion is replaced by a single electron and it is expected that the Na distances will change. We calculated the Na_4^{+3} spectra in the 2.65 <d< 2.40 Å range and found a significant shift of the spectral features which amounts to approximately 1 eV. The overall trend is that an increase in cluster size red shifts the spectrum. Using the model-d charge distribution we optimized the sodium distances to d= 2.60 Å to obtain closest agreement with the experimental spectrum. Absorption measurements on single crystals using polarized light would provide more detailed data that will make it possible to refine the theoretical model.

Acknowledgments.

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Figure Captions

Fig. 1: The halogen-sodalite cage. Regularly alternating Al and Si atoms positioned at the vertices of a truncated octahedron are connected by oxygen atoms (not explicitly shown in the figure). The center of the cage is occupied by a halogen ion surrounded by four Na ions forming a tetrahedron.

Fig. 2: The apparatus for the deposition of alkali metals on the zeolite surface.

Fig.3: Diffuse reflectance spectra of the Na doped $Na_3[AlSiO_4]_3$ sodalite in the 220-850 nm region. The ordinate is $-\log(I/I_0)$ where I is the intensity of the light reflected from the sample and I_0 is the intensity of the light reflected from the $BaSO_4$ reference powder.

Fig. 4: Calculated absorption cross section (in arbitrary units) of the isolated (hypothetical) Na_4^{+3} cluster (a); The absorption cross section of the same cluster inside a sodalite cage surrounded by the "empty" $Na_3[AlSiO_4]_3$ sodalite cages. The spectrum was calculated for particular light polarization with respect to the sodalite single crystal (b); the absorption cross section averaged over all orientations, (c). In all calculations the 2.401 Å for the Na atom - center the cage distance was used. The cage potential was computed using the model-d charges listed in Table I.

Fig. 5: Corrected absorption spectra of the blue (1:4), purple(1:2), and black (>1:1) $Na_4[AlSiO_4]_3$ /$Na_3[AlSiO_4]_3$ samples from the Fig. 2. The spectra were corrected for the color center absorption of the Na_4^{+3} clusters in the $Na_4[AlSiO_4]_3$ /$Na_3[AlSiO_4]_3$ sodalite by subtracting the absorption curve corresponding to the light blue sample (1:10) from the absorption curves of the samples with higher $Na_4[AlSiO_4]_3$ /$Na_3[AlSiO_4]_3$ ratio. Before each subtraction the overall intensity of the (1:10) curve was appropriately normalized.

Fig. 6: One dimensional cuts through the potential energy surface (solid line measured in eV) felt by the excess electron and through the 3-D ground state wave function (dashed line, measured in arbitrary units) of the electron. Two different cut directions are shown: (a) the cut along the 4-fold rotation axis (through the 4-metal rings) and (b) the cut is along the 3-fold rotation axis (through the 6-metal rings). The asymmetry in (b) is due to the orientation of the Na_4 group in conjunction with the 6-metal ring. The ground state energy in this

case is -5.00 eV.

Fig. 7: The high resolution absorption spectra of the b,c,d, and e-model sodalite with the corresponding charges of the framework ions listed in Table I. The fixed value of d=2.401 Å corresponding to the distance of the sodium atoms from the middle of the cage was used in all calculations.

Table I. Various charge distribution schemes for the zeolite framework used to calculate the absorption cross section of the Na_4^{+3} clusters in $Na_3[AlSiO_4]_3$ sodalite.

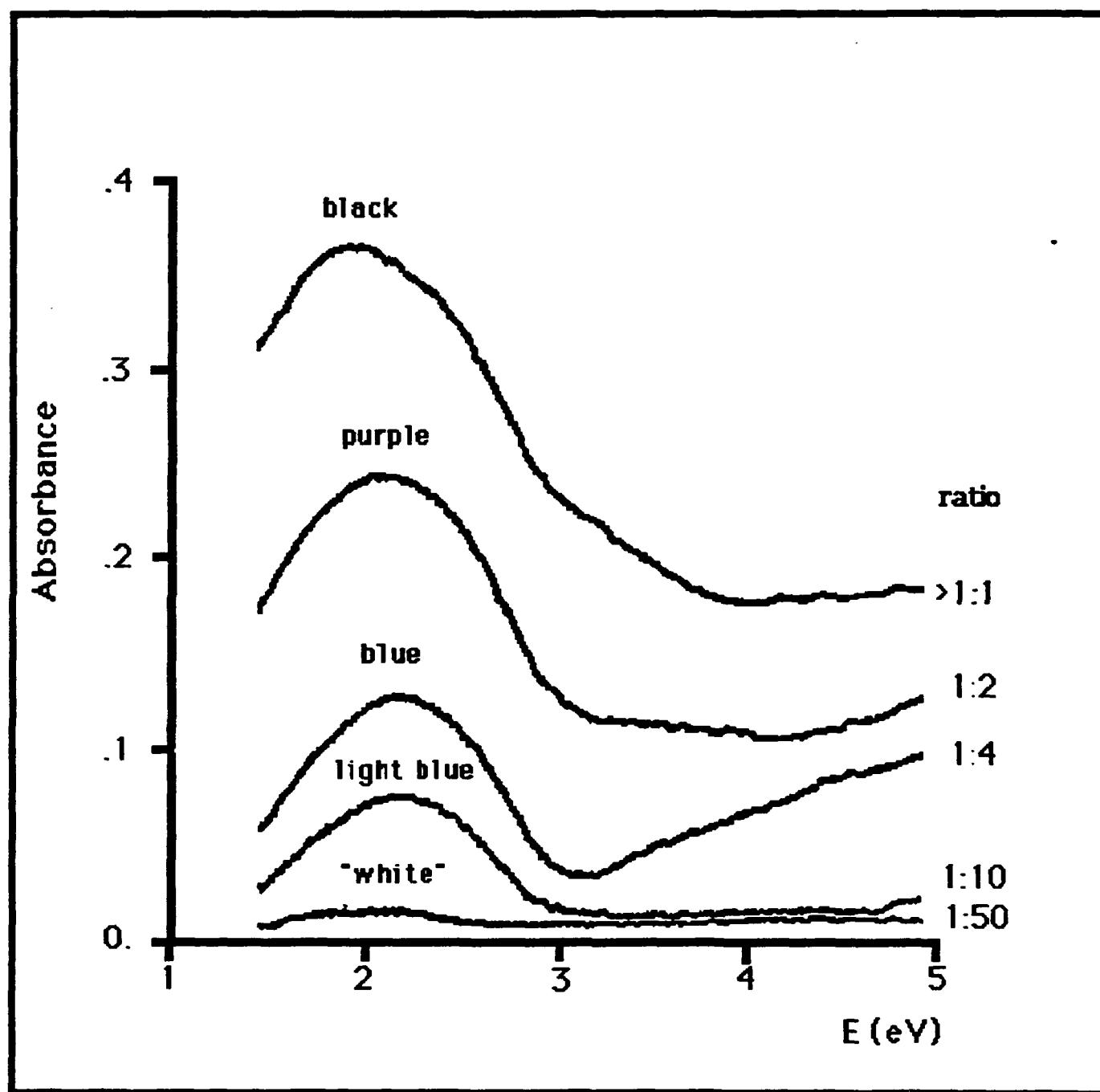| Model	a	b	c	d	e
Na	+1.0	+1.0	+1.0	+1.0	+1.0
Si	0.0	+1.0	+1.5	+1.9	+2.2
Al	0.0	+0.8	+0.85	+0.9	+1.3
O	-0.25	-0.7	-0.8375	-0.95	-1.125
P	**0.99**	**0.98**	**0.97**	**0.95**	**0.05**

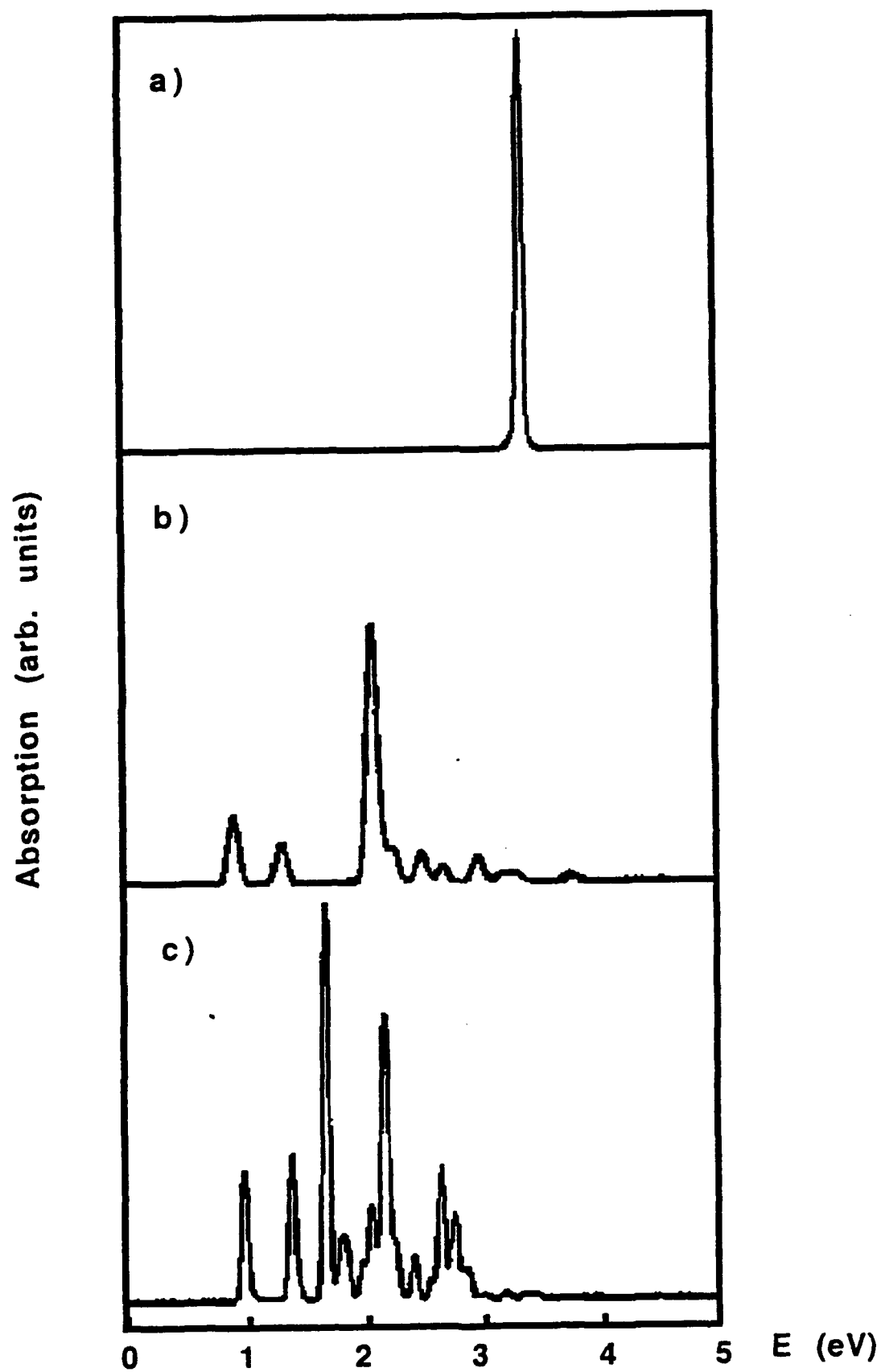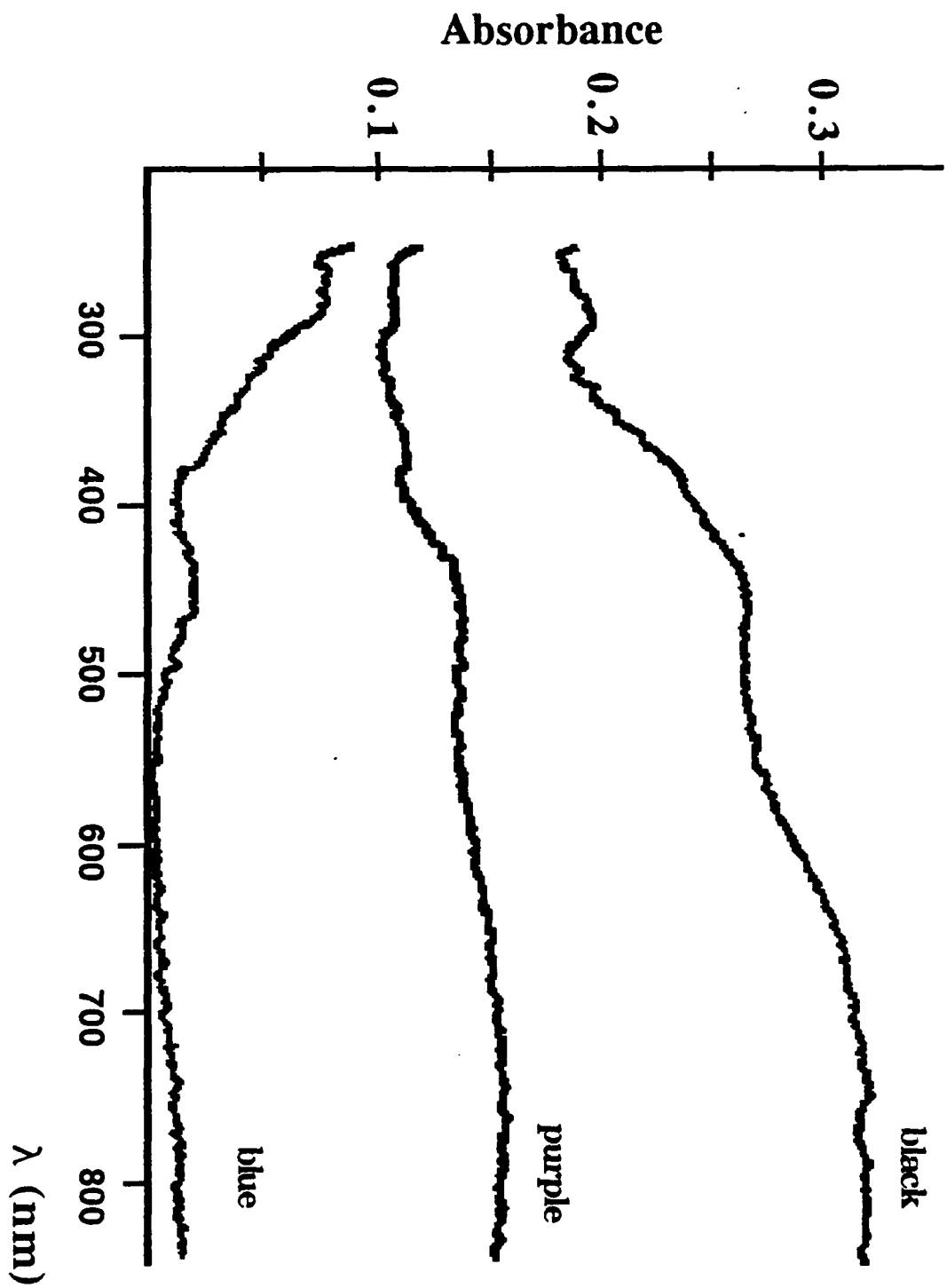sodium

halogen

Fig 1

Fig 2.

Fig 4.

Fig. 5.

Fig 6.

E (eV)
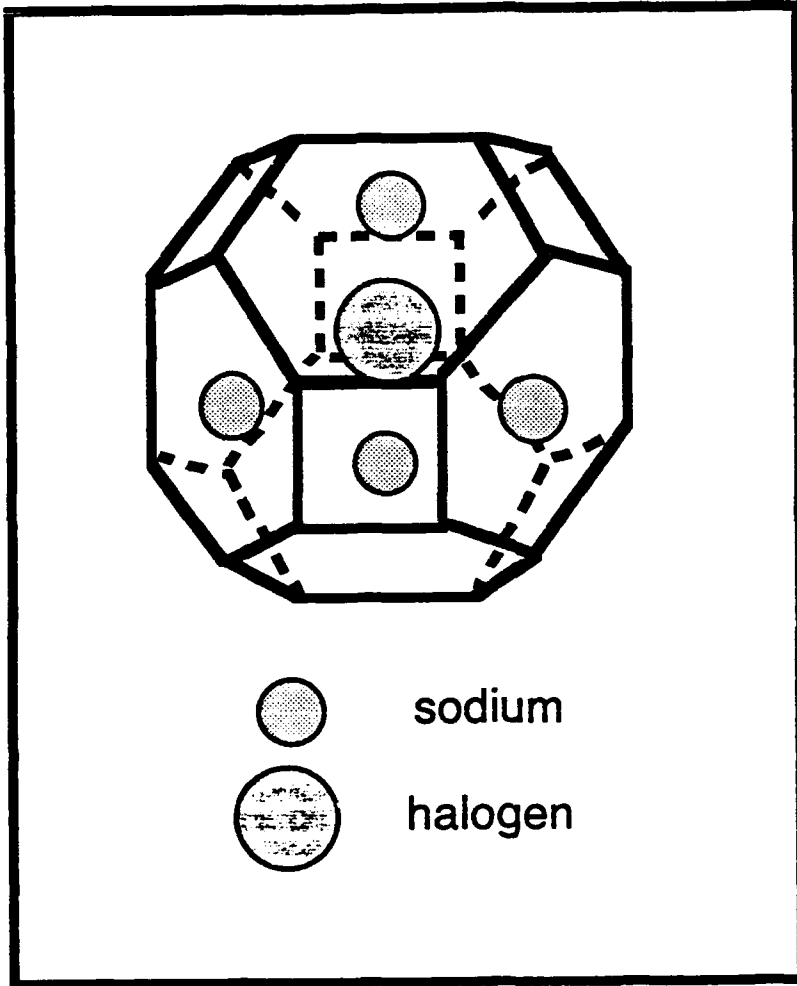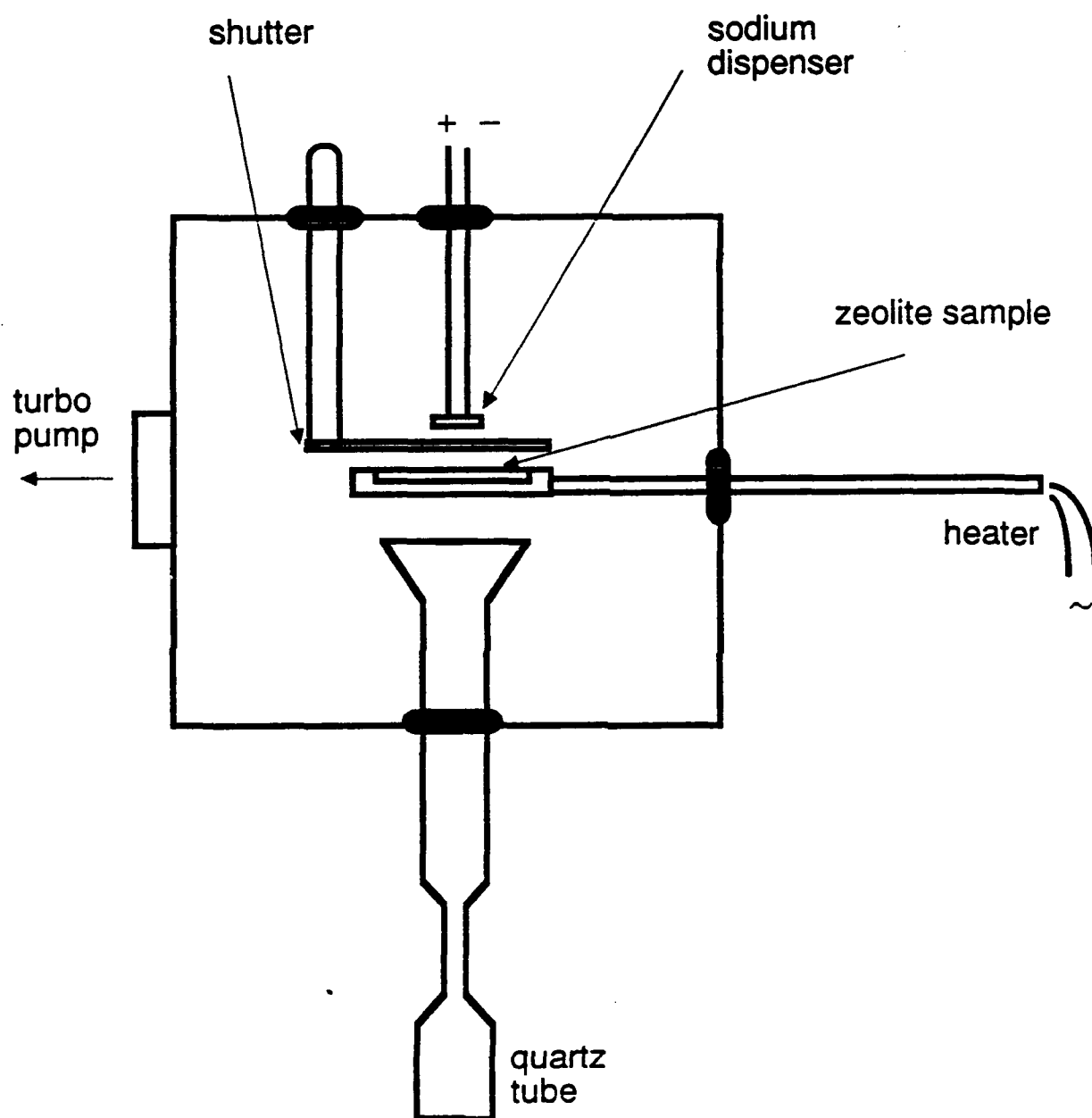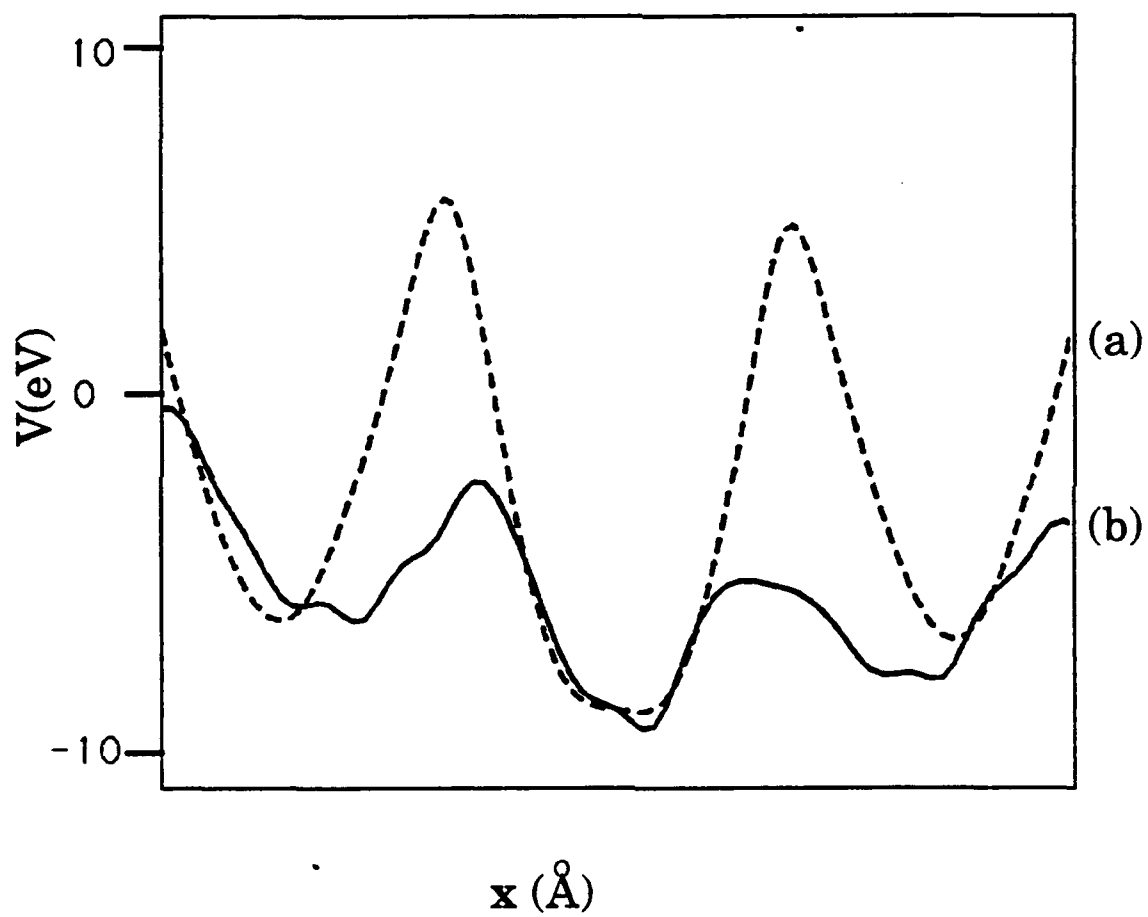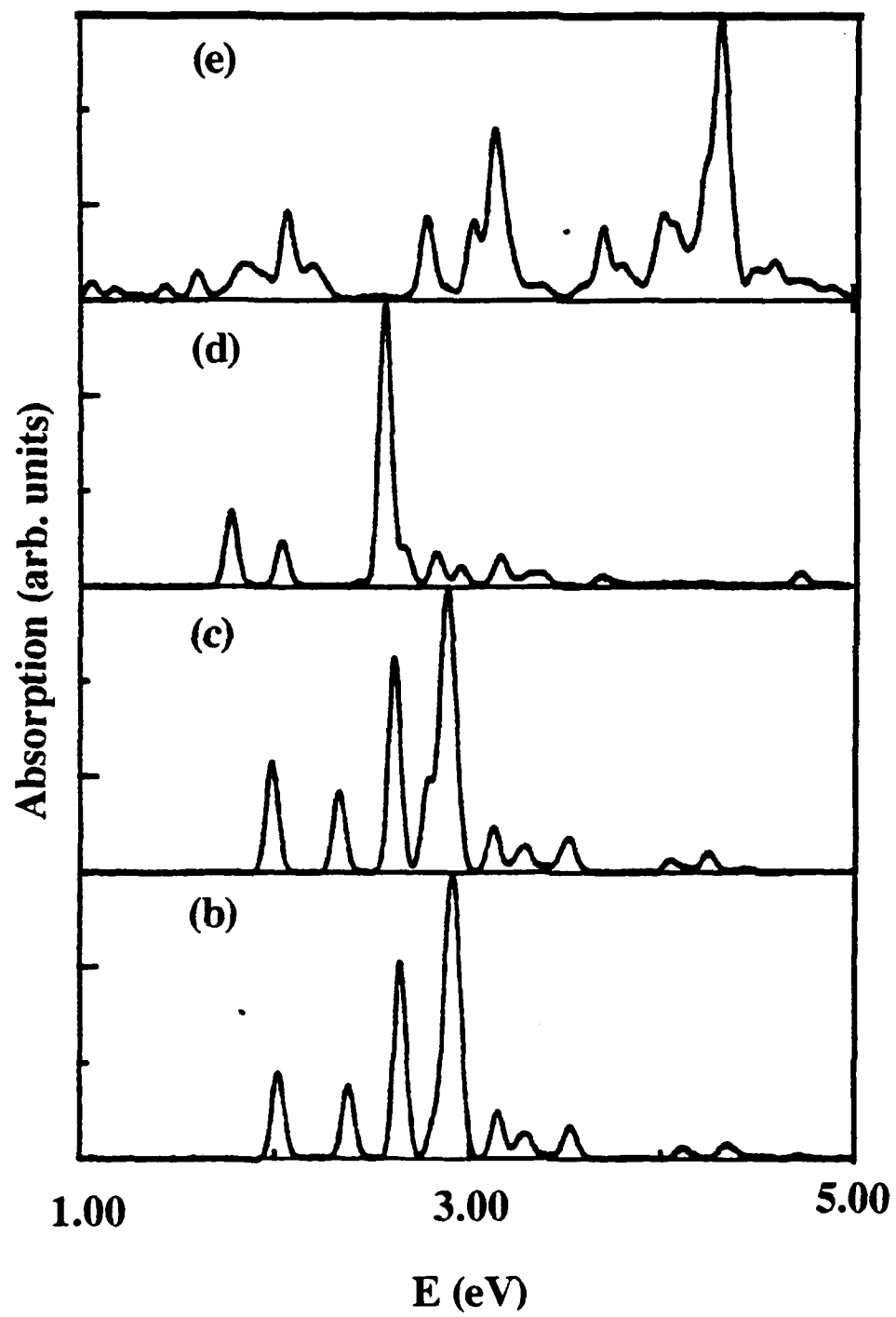
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